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54 Core-shell polymers and compositions containing core-shell polymers.

57 A core/shell polymer comprises a rubbery core of crosslinked, conjugated diolefin polymer or copolymer with 0 or upto 50%, based on the total core weight, of a first vinyl monomer copolymerized with the diolefin, and one or more polymer shells, at least one of which shells is a vinylaromatic polymer or copolymer, the particles further having an average particle diameter no more than 250 nanometers and toluene swell index of from 13 to 45, preferably from 15 to 25.

The core/shell polymers are useful for modifying the properties of olefinic, aromatic addition and/or condensation resins, particularly poly(styrene).

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CORE-SHELL POLYMERS AND COMPOSITIONS CONTAINING CORE-SHELL POLYMERS

This invention is concerned with core/shell polymers which are especially, though not exclusively, suitable for modifying the impact properties of styrenic resins. The present invention is also concerned with compositions containing the core/shell polymers, more particularly with aromatic and olefinic resins which contain the core/shell polymers, for example butadiene-styrene impact modifiers.

Commercial high-impact polystyrene (HIPS) is typically prepared by continuous bulk polymerization with rubbery polybutadiene impact modifiers. During the polymerization the modifiers form domains about 2-5 micrometers in diameter within the polymer. Although tougher than unmodified polystyrene, such HIPS has a poorer balance of impact strength, surface gloss and mechanical properties than competing resins such as acrylonitrile-butadiene-styrene (ABS), and has poorer environmental stress-craze resistance to food oils. The high viscosities generated by high loading of polybutadiene and by the conditions required for proper concurrent polymerization of the polystyrene matrix polymer limit the property balance obtained by this process, so that high impact resistance, high gloss and high strength are difficult to obtain in a single, bulk polymerization.

Impact modifiers considered useful by the prior art for improving impact resistance of polystyrene have particle sizes greater than two micrometers. C. B. Bucknall, Toughened Plastics, Applied Science, London, 1977, states that emulsion polymers having particle sizes substantially smaller than one micrometer are unsuitable for making HIPS. More recently J. Silberberg et al., Journal of Applied Polymer Science, Vol. 22, pages 599-609 (1978) reported that the threshold particle size for an effective polystyrene modifier is above one micrometer, and preferably 2-5 micrometers. A. M. Donald et al., Journal of Applied Polymer Science, Vol. 27, pages 3729-3741 (1982) actually advocates removal of all modifier particles smaller than one micrometer in diameter for most efficient toughening of polystyrene, as such particles are considered to be ineffective diluents. Although Hobbs, European Patent Publication EP-A-158,258, teaches grafting small (below 1000 nm) rubber particles to polystyrene chains and incorporating the resulting modified styrene polymer with a styrene polymer containing larger (3-10 μm) particles of rubbery impact modifier, Damen, EP-A-143,500, teaches that using bimodal size distribution of the modifiers sacrifices gloss for superior impact strength.

Damen, above, does teach that domains of rubbery impact modifier smaller than 250 nm may be introduced into poly(styrene) by an elaborate process of block copolymerizing the rubber monomer with a styrenic monomer, solubilizing the copolymer in styrene monomer, and bulk polymerizing the solution. Phase inversion in the polymerizing system precipitates the small domains of rubber throughout the poly(styrene) to produce a resin with an adequate balance of gloss and impact strength.

Additive impact modifiers have been used to improve physical properties in HIPS. Typically, these are made by anionically polymerizing styrene and butadiene to form block copolymers having discrete segments of poly(butadiene) and poly(styrene) covalently linked end to end. Such block copolymers are also known as thermoplastic elastomers. Because these copolymers are not covalently crosslinked during manufacture, properties of styrene blends made from them are highly dependent on such processing conditions as shear rate and blending temperature. Such styrene-block copolymer blends have found utility for ignition-resistant resins, but they are not considered economical for most other uses, and their resistance to chemical attack is little better than that of conventional HIPS.

For a discussion of block copolymers, their structure, physical properties and other characteristics, that will assist in understanding the difference between such polymers and the polymers of the invention set forth below, one may consult, for instance, Aggarwal, "Structure and Properties of Block Polymers and Multiphase Polymer Systems: an Overview of Present Status and Future Potential," Polymer, Vol. 17, pp. 938-956 (November, 1976).

Other uses of block copolymers as impact-property modifiers for poly(styrene) are disclosed by Miller, US-A-4,308,358, in which a bulk-polymerized block copolymer is melt blended with poly(styrene), and Russell, US-A-4,371,663 in which the block copolymer is crosslinked and blended with HIPS. Russell determines the swell index of his copolymers, and observes that as the swell index increases (i.e., polymer crosslinking decreases) the impact resistance of the modified poly(styrene) decreases.

Swell index is also applied to large-particle-size, rubbery impact modifiers by Echte et al, US-A-4,330,641. This patent teaches that stress-cracking resistance is achieved only when particles are larger than 3.5 μm .

Methacrylate-butadiene-styrene (MBS) impact modifiers are well known for modifying poly(vinylchloride) resins, as for example those taught by Goldman, US-A-4,443,585. Such modifiers in recent years have also been found useful for modifying other polymers, such as polycarbonates, crystallizable thermoplastic polyesters, and other engineering resins. Emulsion-polymerized MBS modifiers have been used to modify blends of transparent HIPS with polyphenylene ethers, but the form of these modifiers has been a particle with a large, relatively hard core of polystyrene surrounded by a thin, softer, rubbery shell. Lonning, US-A-3985693, teaches modification of Poly(vinyl chloride) compositions with modifiers which essentially require the presence of acrylonitrile.

It is an object of this invention to provide an additive polymer which is useful in improving the balance of impact strength and other physical properties such as gloss, stiffness and resistance to environmental stress crazing, when blended with aromatic addition and condensation polymers, polyolefins, and blends thereof, including such polymers blended with conventional impact-strength modifiers. The term "additive polymer," as used herein, is intended to mean a polymeric composition useful as an additive to other polymeric compositions. The additive polymer of the present invention is a core/shell polymer.

In accordance with the present invention we provide an additive polymer having a particle size below about 250 nanometers (nm) and comprising a rubbery core of crosslinked, conjugated diolefin polymer or copolymer and one or more shells of polymer, at least one of which shells is a vinylaromatic polymer or copolymer, the additive polymer having a toluene swell index of from about 13 to about 45.

The additive polymer of the present invention is particularly suitable as an additive for modifying the impact properties of aromatic addition and condensation polymers, preferably for styrenic resins such as poly(styrene) or for polyphenylene oxide resins, for polyolefin resins such as polypropylene, and for blends of these and other resins. It may be present in such resins alone or, more preferably, in the presence of other additive polymers such as conventional impact-modifying polymers useful with these resins. These other additional polymers are preferably present at levels of from about 1 to about 30% by weight.

The additive polymers of the present invention have a rubbery core of conjugated diolefin polymer or copolymer, such as polymers or copolymers of butadiene, isoprene, chloroprene and dimethylbutadiene, preferably butadiene. The term "copolymer," as used herein, is intended to mean a polymer produced by copolymerizing two or more monomers that are copolymerizable with one another. A designation of the type of copolymer, such as "conjugated diolefin," "butadiene" or "vinylaromatic," as used herein, is intended to mean that the designated type of monomer formed the largest fraction of monomers in the mixture that was copolymerized, unless otherwise specifically indicated. In the present instance the conjugated diolefin may be copolymerized with a minor amount of one or more copolymerizable vinylic monomers such as vinyl aromatic monomers, for example styrene and alkylstyrene, alkyl acrylates and methacrylates where the alkyl group contains from 1 to 8 carbon atoms, and nitriles such as acrylonitrile and methacrylonitrile. More particularly, at least one of the shells is preferably a vinyl aromatic polymer or copolymer copolymerized from one or more monomers selected from the group consisting of vinyl aromatic monomers, alkyl acrylate monomers having 1 to 8 carbon atoms in the alkyl group, alkyl methacrylate monomers having 1 to 8 carbon atoms in the alkyl group and polyvinyl unsaturated crosslinking monomers, and the remainder of the shells, if present, are preferably vinylaromatic polymers or copolymers or methylmethacrylate polymers or copolymers copolymerized from one or more monomers selected from the group consisting of vinyl aromatic monomers, methylmethacrylate, alkyl acrylate monomers having 1 to 8 carbon atoms in the alkyl group and polyvinyl unsaturated crosslinking monomers. In a preferred embodiment, the first alkyl acrylate is ethylacrylate and the vinyl aromatic copolymer is a copolymer with methylmethacrylate. The preferred percentage of this vinylic monomer is from zero or upto about 50% by weight, these percentages being based upon the total weight of the diolefin and any other vinylic monomer used to prepare the rubbery core polymer.

This core polymer is typically crosslinked, either by copolymerizing with a crosslinking monomer or through crosslinking which results from selection of suitable polymerization conditions. Such a selection of conditions involves selecting temperatures, initiators, presence or absence and type of chain regulating agents, and the like, in a manner well known to those skilled in the art. Crosslinking monomers are similarly well known and comprise polyethylenically unsaturated monomers such as divinylbenzene, trivinylbenzene, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, trimethylolpropane trimethacrylate and many others which will be apparent to those skilled in the art. Crosslinking is critical to the effectiveness of the composition as an impact modifier, as it acts to maintain the structural integrity of the modifier during processing and fabrication steps performed on the polymer. As crosslinking may not be readily measured directly, a secondary parameter, the toluene swell index, which relates to the degree of crosslinking, is used herein to define the crosslink density of the composition. This parameter is the ratio of toluene-swollen polymer weight to dried polymer weight for a given sample. The crosslink density of the core polymer must

be controlled such that the toluene swell index of the finished core-shell particle is from about 13 to about 45, preferably from about 15 to about 25. The effectiveness of such a lightly crosslinked impact modifier is especially surprising in view of the teaching of Russell, above, that increased crosslinking (lower swell index) improves impact resistance.

6 Surrounding the rubbery core polymer are one or more polymer shells of at least one of which is a shell of vinylaromatic polymer or copolymer such as styrene or alkylstyrene, e.g., alpha-methylstyrene, polymer or copolymer. The shell may be a copolymer of vinylaromatic monomer and alkyl acrylate and/or methacrylate monomer, the alkyl group having from 1 to 8 carbon atoms, for example ethyl acrylate and/or methyl methacrylate. The ratio of core polymer to shell polymer is preferably from about 30:70 to about 10 95:5 by weight, based on the total core and shell weight. The more preferred core-to-shell ratio is from about 60:40 to about 80:20. One or more of the shells may be crosslinked by copolymerizing them with polyvinyl unsaturated crosslinking monomers. One or more of the shells may optionally be grafted to the core and/or to one another.

The optional shells may comprise vinylaromatic polymers or copolymers, or methyl methacrylate 15 polymers or copolymers, including copolymers with alkyl acrylates having 1 to 8 carbon atoms, such as ethyl acrylate. The other copolymerizable monomers may be present with the methyl methacrylate in the monomer mixture that is polymerized to make the optional additional shells at levels of from 0 to 99% by weight, based on the total weight of methyl methacrylate and other copolymerizable monomers. The optional additional shells may comprise from zero or upto about 25% by weight, of the total weight of core, 20 and shells, and may be similarly crosslinked.

The additive polymers of the present invention are especially small; their particle diameter is about 250 nm or smaller, preferably from about 50 to about 250 nm, and more preferably from about 150 to about 200 nm. Any suitable method, such as emulsion polymerization, may be used for preparing particles of that size having the required core-shell structure. If the additive polymers are made by emulsion polymerization, the 25 polymerization may be conducted such that the resulting latex particles will inherently have a narrow distribution of particles diameters.

The particles of the present invention are significantly smaller than typical modifiers used with polystyrene to make HIPS, and appear to function synergistically with the larger modifier particles. They produce an observable but significantly smaller improvement in the impact resistance of styrene homo- 30 polymer than of HIPS.

The additive polymers of the present invention, in addition to being useful for improving the physical properties of HIPS and other styrenic polymers, are also useful in improving the physical properties of blends of HIPS with other compatible polymers or copolymers, including polyolefins and aromatic condensation polymers such as polyphenylene oxides. They also improve the physical properties of unmodified 35 polystyrene and other aromatic addition and condensation polymers, of copolymers of styrene and other vinylaromatic monomers with other monomers such as acrylic and methacrylic monomers, unsaturated carboxylic acid and anhydride monomers such as maleic anhydride, and nitriles such as acrylonitriles. They also improve the physical properties of polyolefins, as for example polypropylene.

Accordingly, in accordance with a further aspect of the present invention we provide a composition 40 which comprises a continuous phase of olefinic, aromatic addition and/or condensation polymer or copolymer, and a first discontinuous phase of domains having a diameter no more than 250 nm and comprising a rubbery core of crosslinked, conjugated diolefin polymer or copolymer, with 0 or upto 50%, based on the total core weight, of a first vinyl monomer copolymerised with the diolefin, and one or more shells of polymer, at least one of which is a vinylaromatic polymer or copolymer, the discontinuous phase 45 being introduced into the continuous phase as core-shell polymer particles of the invention. Preferably, the composition additionally comprises from 1 to 30% by volume of a second discontinuous phase of domains of crosslinked and grafted rubbery poly(butadiene) modifier, the domains of the second discontinuous phase preferably having an average diameter from 0.05 to 20 micrometers. Preferably the aromatic addition or condensation polymer or copolymer is a vinylaromatic addition polymer or copolymer or a polyphenylene oxide polymer or copolymer, and is preferably a styrenic polymer or copolymer, more preferably poly- 50 (styrene) or a copolymer thereof.

Those skilled in the art will understand the term "domain" to mean a polymeric material included in, but distinguishable from, the matrix polymer.

The present invention further includes a method of making the core/shell polymers and compositions 55 containing the core/shell polymer.

The following examples are intended to illustrate, but not limit, the present invention. All proportions are by weight unless otherwise noted, and all reagents are of good commercial quality.

Polymer blends described in the following examples were prepared by mixing the matrix polymer and the modifier during melt extrusion in a counter-rotating American Leistritz 33-mm twin-screw extruder at a throughput rate of 100 g per minute, using a die melt temperature of 200-220°C for modified polystyrenes, 225-230°C for blends containing polypropylene and 250-260°C for blends containing polyphenylene oxide (PPO). The molten extrudate was collected as a strand which was cooled in a water bath and cut into pellets.

Test specimens were prepared by loading the test pellets into a 28-g-capacity, Newbury Industries reciprocating-screw injection molding machine operating at a melt temperature of 230-250°C for modified polystyrenes, 220-225°C for modified polypropylenes and 295-300°C or polymers containing PPO, and injecting the test polymer into chrome-plated mold cavities cut to ASTM specifications and heated to 43-49°C for modified polystyrene and polypropylene, or 91-93°C for blends containing PPO. Test specimens were conditioned according to ASTM D618, Procedure A.

The following tests were used to evaluate the properties of polymers in the examples below:

Notched Izod impact strength was determined using 3.2 × 12.7 × 63.5-mm (1/8 × 1/2 × 2.5 inch) test specimens according to ASTM Standard Procedure D256.

Falling-dart impact strength was determined using a Dynatup[®] instrumented drop tower manufactured by Effects Technology, Inc. Test specimens of 50.8 × 76.2 × 3.2 mm (2 × 3 × 1/8 inch) were clamped onto a support ring 31.8 mm (1 inch) in diameter and struck at a velocity of 305 cm/sec with an instrumented dart having a tip diameter of 12.7 mm (1/2 inch). The energy absorbed by the sample up to the point of tear-through by the dart was integrated, and an average of at least three impacts was reported.

Tensile strength was determined using a 2.54-mm-thick microtensile specimen according to ASTM Standard Procedure D638, using a strain rate of 100% elongation per minute.

Surface gloss was measured using 50.8 × 76.2 × 3.2-mm (2 × 3 × 1/8 inch) injection-molded plaques using a Gardner Glossmeter and an incident angle of 60°.

Toluene swell index was determined using a small sample of dried modifier, typically 0.15 - 0.25 g, weighed into a glass vial and covered with about 45 ml of commercial-grade toluene. The sample was allowed to stand covered for three days at room temperature to allow full equilibration, and the swollen sample was then quickly filtered from the toluene and weighed. The wet sample was then carefully dried in a vacuum oven at 80°C and reweighed. The swell index was calculated by dividing the weight of the swollen sample by that of the dried sample.

Environmental stress-craze resistance (ESCR) was determined using injection-molded test specimens prepared as for the Notched Izod impact strength test. The bar was clamped in a fixture having a radius such that the outer surface of the bar was subjected to 1% strain. The clamped bar was then immersed in the indicated crazing agent, as for example, a 50/50 mixture of cottonseed oil and oleic acid, for 24 hours. The flexural strength of the bars, and of control bars held in 1% strain in air, was measured according to ASTM Standard Procedure D790, and the ESCR was calculated by dividing the average flexural strength of the test bars by that of the control bars.

Emulsion particle sizes were measured by use of a Nanosizer[®] instrument manufactured by Coulter Electronics. This instrument estimates the average size of emulsion polymer particles by following the light scattered by the Brownian motion of the emulsion.

EXAMPLE 1

This example illustrates a method for preparing the modifiers of the present invention; in this three-step procedure the rubbery core polymer is formed as a latex (Step A) the particle size of the latex is increased by controlled destabilization or agglomeration (Step B), and an outer shell is grafted onto the agglomerated core polymer (Step C).

Step A

The following were charged to a stainless steel reactor:

Butadiene	75 parts
Styrene	25 parts
Potassium Oleate	5 parts
n-Dodecyl Mercaptan	0.5 parts

Potassium Persulfate 0.3 parts
 Deionized Water 180 parts

The reactor was heated with stirring to 50°C and held at that temperature for 24 hours. The final conversion to polymer was at least 95%.

Step B

The following were charged to a glass flask:

Rubber Latex of
 Step A 100 parts
 Water 140 parts

The flask contents were stirred and adjusted to pH 4.5 with acetic acid (approximately 2 parts), then to pH 10 with sodium hydroxide (approximately 5 parts).

Step C

A glass flask was charged with 80 parts of the wet, agglomerated rubber latex of Step B. The flask contents are heated to, and maintained at, 50°C with stirring, and the following are charged to the flask:

Styrene 20 parts
 Sodium Formaldehyde
 Sulfoxylate 0.06 parts
 (Ethylenedinitrilo)
 tetraacetic acid,
 disodium salt 0.006 parts
 Ferrous Sulfate 0.0012 parts
 Water 510 parts

To the resulting mixture 0.063 parts of *tert*-butyl hydroperoxide was added over a period of two hours. The final conversion to polymer was at least 99%, and the final emulsion particle size was 190 nanometers (nm), as measured by Nanosizer. The resulting modifier polymer was stabilized with 2,6-di-*tert*-butyl-4-methylphenol, marketed as Ionol, and was isolated by salt coagulation. The dried modifier had a toluene swell index of 19. The modifier had the following overall composition:

Bd / Sty
 60 / 40

It is understood that the above example represents only one method for preparing the additive polymer of the present invention. Other methods known to those skilled in the art may be used, as for example that of Goldman, U.S. Patent No. 4,443,585, which is hereby incorporated into the present specification, provided that the reaction conditions are controlled as discussed above to yield polymers having a toluene swell index within the range of the present invention.

EXAMPLE 2

This example illustrates the improvement in impact strength obtainable using the modifiers of the present invention. Notched Izod impact strength was determined for an unmodified HIPS (a general-purpose, medium-impact, injection-molding grade of HIPS prepared by conventional bulk polymerization and marketed as Styron 489 by Dow Chemical) and for the same HIPS modified at 20% loading with comparative, conventional modifiers of the prior art, block copolymer modifiers of the prior art, and the modifiers of the present invention. The conventional MBS modifiers are crosslinked core-shell polymers typically employed for physical-property modification of poly(vinyl chloride). Modifier A has a rubbery core of poly(butadiene) grafted with a copolymer of styrene and methyl methacrylate, Modifier B has a rubbery core of butadiene-butyl acrylate copolymer grafted with a copolymer of styrene and methyl methacrylate, and Modifier C, a commercial modifier marketed as Metablen C-223 by Mitsubishi Chemical Industries, Ltd., has a rubbery core of poly(butadiene) agglomerated to a larger particle size and subsequently grafted with a copolymer of styrene and methyl methacrylate. The modifier of the present invention may be prepared according to the procedure of Example 1; the particular modifier used has the overall composition:

Bd / Sty
62.5/37.5

and is identified in Table I as Modifier D. Izod impact values were determined using a 3.2 -mm notched specimen at 23°C.

TABLE I

Modifier	Modifier Type	Notched Izod		
		Impact Value, Joules/Meter	Swell Index	Particle Size, μ m
None	Matrix Polymer	101	----	----
A	Conventional MBS	117	10.5	0.2
B	Conventional MBS	123	10.5	0.2
C	Conventional MBS	171	11.3	0.5
D	Present Invention	438	23	0.18

EXAMPLE 3

This example illustrates the effectiveness of the modifiers of the present invention for toughening filled matrix polymer. The modifier may be prepared according to the procedure of Example 1, and has an overall composition of 60 parts butadiene, 36 parts styrene and 4 parts methyl methacrylate; it has a swell index of 14 and a particle size of 0.18 μ m. This modifier was blended at 20% loading with the HIPS described in Example 2 and the indicated levels of the indicated fillers, and notched Izod impact strength was determined for the resulting blends at 23°C for 3.2 mm and 6.4 mm notches. The fillers used were calcium carbonate, marketed as Winnofil S by ICI Americas, Inc. talc, marketed as Mistron by Cyprus Industrial Minerals Co., and wollastonite, marketed as Wollastakup G by Nyco Products Co. The results of these determinations are shown in Table II.

TABLE II

Filler Loading and Type	Notched Izod Impact Strength, Joules/Meter at 23°C	
	3.2 mm	6.4 mm
No Filler, Unmodified	155	144
No Filler, Modified	358	262
10% CaCO_3	235	64
20% CaCO_3	64	43
10% Talc	165	101
20% Talc	64	48
10% Wollastonite	192	181
20% Wollastonite	139	133

EXAMPLE 4

This example illustrates the effectiveness of the modifiers of the present invention for improving the toughness of clear, unmodified styrenic polymers. The modifier used is the one used in Example 2. Two clear, unmodified matrix polystyrene polymers were blended with this modifier: a general-purpose, injection-molding grade of clear, unmodified polystyrene homopolymer marketed as Styron 666 by Dow Chemical Company, and a clear, unmodified copolymer of styrene and a minor amount of methyl methacrylate marketed as NAS by Richardson Polymer Corp. Improvement of the impact strength is shown for various loadings of modifier in Table III.

TABLE III

Modifier Loading	Matrix Polymer	Notched Izod Impact Strength, J/m at 23°C	
		3.2 mm	6.4 mm
0	666	11±5	11±5
20%	666	11±0	21±0
30%	666	27±5	21±0
40%	666	37±5	32±5
0	NAS	11±5	11±0
20%	NAS	21±0	27±5
30%	NAS	48±21	32±11
40%	NAS	75±11	107±27

As may be seen from these results, the modifier of the present invention is less effective at improving toughness of clear, unmodified styrene polymers, but it nevertheless produces significant toughness improvement while maintaining very high gloss.

EXAMPLE 5

This example illustrates that the modifiers of the present invention are effective at improving impact strength of HIPS matrix polymers containing minor amounts of other comonomers. The modifier of the present invention has a composition of 60.6 parts butadiene, 36.4 parts styrene and 3.0 parts methyl methacrylate, and has a swell index of 15.5 and a particle size of 0.17 μ m. The matrix polymer used in this example is a HIPS type polymer containing approximately 10-16% copolymerized maleic anhydride, marketed as Dylark 350 by Arco Chemical Co. The results are shown in Table IV.

TABLE IV

Modifier Loading	Notched Izod Impact Strength J/m at 23°C		Dynatup Dart Impact Strength, Joules at 23°C
	3.2 mm	6.4 mm	
0	112	101	
11.7±4.3			
5%	123	107	14.5±3.9
10%	149	123	19.2±1.6
15%	181	139	25.5±3.0

EXAMPLE 6

This example illustrates that the modifier of the present invention is effective at improving the impact strength of polystyrene blended with other compatible thermoplastics, such as polyphenylene ethers. In Table V the results of modifying such blends with conventional MBS modifiers and with modifiers of the present invention are shown. The modifier of the present invention has a composition of 62.5 parts butadiene and 37.5 parts styrene; it has a swell index of 13.4 and a particle size of 0.18 μ m. The matrix polymer is a blend of polystyrene, poly(2,6-dimethyl-p-phenylene oxide) and a mineral filler; the blend is marketed as Noryl HS-2000 by General Electric Co. The conventional modifiers are those described in Example 2.

TABLE V

Modifier	Loading	Modifier Type	Notched Izod Impact Strength, J/m	
			3.2 mm	6.4 mm
None	0	-----	96	91
	5%	Present Invention	263	167
"A" of Ex. 2	5%	Conventional MBS Modifier	224	139
"B" of Ex. 2	5%	Conventional MBS Modifier.	230	149

EXAMPLE 7

This example illustrates the effectiveness of the modifiers of the present invention in improving the resistance of HIPS polymers to environmental stress crazing (ESCR). The action of food oils, such as butter or oleic acid-cottonseed oil mixtures on HIPS is to degrade tensile strength and impact resistance, especially when the surface of the HIPS is held under tensile strain. Table VI shows ESCR values for each of three HIPS materials at various loadings of Modifier D from Example 2 when exposed to butter for 24 hours at room temperature. The matrix polymers are a general-purpose, medium-impact-strength, injection-molding grade of HIPS prepared by conventional bulk polymerization and marketed as Styron 489, a general-purpose, low-impact, extrusion grade of HIPS marketed as Styron 484, both by Dow Chemical Co., and an extra-high-impact HIPS marketed as Hostyren 840 by American Hoechst Corp.

TABLE VI

Modifier Loading (Strength) Weight %	ESCR Rating (% Retention of Flexural Resin)		
	Styron 484	Styron 489	Hostyren 840
0	68%	50%	15%
10	86%	97%	87%
20	91%	97%	---

EXAMPLE 8

This example illustrates that the modifier of the present invention may be used to improve the balance of properties obtained with blends of HIPS and clear, unmodified polystyrene. As is shown in Table VII, impact strength is improved while ESCR, tensile strength and gloss are maintained at high levels. The clear, unmodified polystyrene used in this example is a general-purpose grade, and the HIPS materials are a medium-impact, injection-molding grade polymer marketed as 4324 and an extra-high-impact, extrusion-grade resin marketed as 7500, both by Mobil Chemical Co. The modifier of the present invention has a composition of 62.5 parts butadiene and 37.5 parts styrene; it has a swell index of 16.3 and a particle size of 0.17 μ m.

TABLE VII

HIPS Resin	Wt% Modifier	Wt % Crystal Polystyrene	3.2 mm Izod, 23°C J/m	Gloss 60°	Tensile Stress, MPa	Yield Stress, MPa	%ESCR 24 Hrs
4324	0	0	91	75	24		*
4324	15	0	198	78	28		54
4324	15	15	181	85	30		*
4324	15	30	144	85	31		*
7500	0	0	133	47	26		64
7500	15	0	299	61	25		86
7500	15	15	272	70	28		82
7500	15	30	235	74	31		54

* - samples fractured during immersion in cottonseed oil/oleic acid

EXAMPLE 9

The preceding examples show that the modifiers of the present invention are effective in modifying polystyrenes, related copolymers and blends thereof. This example illustrates that the modifiers of the present invention are also surprisingly effective at modifying polypropylene. As shown in Table VIII, a modifier of the present invention, the modifier of Example 8, is effective at improving the ductility of polypropylene, as measured by the tensile elongation to breakage test and impact strength measured by both the notched Izod impact test and Dynatup dart impact test. Prior art MBS modifiers, such as MBS modifier A as described in Example 2 are significantly less effective than modifiers of the present invention.

In the example, the modifiers were melt blended with a general-purpose, medium-flow grade of polypropylene homopolymer, marketed as Pro-Fax 6323 by Himont. Modifiers of the present invention are also expected to be useful in modifying polypropylene copolymers, as well as blends of polypropylenes and styrenic resins.

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Table VIII				
10 <u>Modifier</u>	<u>Loading weight%</u>	<u>Tensile Elongation to Break, %</u>	<u>Notched Impact J/m at 23°C</u>	<u>Dynatup Impact J at 23°C</u>
None	0	11	11	0.31±.03
Present				
15 Invention	40	>260	27	4.6±2.2
Conventional				
MBS A of Ex. 2	40	20	5	0.19±.04

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Claims

1. A core/shell polymer suitable for modifying the impact-properties of poly(styrene) comprises a
25 rubbery core of crosslinked, conjugated diolefin polymer or copolymer with 0 or upto 50%, based on the total core weight, of a first vinyl monomer copolymerized with the diolefin, and one or more polymer shells, at least one of which shells is a vinylaromatic polymer or copolymer, the particles further having an average particle diameter no more than 250 nanometers and a toluene swell index of from 13 to 45, preferably from 15 to 25.
- 30 2. A polymer as claimed in claim 1, wherein the average particle diameter is from 50 to 250 nanometers, preferably from 150 to 200 nanometers.
3. A polymer as claimed in claim 1 or claim 2, wherein the conjugated diolefin is butadiene, isoprene, chloroprene and/or dimethylbutadiene.
4. A polymer as claimed in any one of the preceding claims, wherein the first vinyl monomer is
35 styrenic, e.g. styrene, and/or a first alkyl acrylate and/or methacrylate, the alkyl group having from 1 to 8 carbon atoms.
5. A polymer as claimed in claim 4 wherein the first alkyl acrylate and/or methacrylate is methylmethacrylate and/or ethyl methacrylate and/or butyl methacrylate.
6. A polymer as claimed in any one of the preceding claims, wherein the vinylaromatic polymer or
40 copolymer is a polymer or copolymer of styrene and/or alkylstyrene, the alkyl group having from 1 to 8 carbon atoms.
7. A polymer as claimed in anyone of the preceding claims, wherein the vinylaromatic copolymer is a copolymer of a second alkyl acrylate and/or methacrylate, the alkyl group having from 1 to 8 carbon atoms.
8. A polymer as claimed in claim 7, wherein the second alkyl acrylate and/or methacrylate is methyl
45 methacrylate and/or ethyl acrylate.
9. A composition which comprises a continuous phase of olefinic, aromatic addition and/or condensation polymer or copolymer, and a first discontinuous phase of domains having a diameter no more than 250 nm, and comprising a rubbery core of crosslinked, conjugated diolefin polymer or copolymer, with 0 or upto 50% based on the total core weight, of a first vinyl monomer copolymerised with the diolefin, and one or
50 more shells of polymer, at least one of which is a vinylaromatic polymer or copolymer, the discontinuous phase being introduced into the continuous phase as core-shell polymer particles as claimed in any one of claims 1 to 7.
10. A composition as claimed in claim 9, wherein the composition additionally comprises from 1 to 30%
55 by volume of a second discontinuous phase of domains of crosslinked and graftlinked rubbery poly-(butadiene) modifier, the domains of the second discontinuous phase preferably having an average diameter from 0.05 to 20 micrometers

11. A composition as claimed in claim 9 or 10 wherein the aromatic addition or condensation polymer or copolymer is a vinylaromatic addition polymer or copolymer or a polyphenylene oxide polymer or copolymer, and is preferably a styrenic polymer or copolymer, more preferably poly(styrene) or a copolymer thereof.

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54 **Core-shell polymers and compositions containing core-shell polymers.**

57 A core/shell polymer comprises a rubbery core of crosslinked, conjugated diolefin polymer or copolymer with 0 or upto 50%, based on the total core weight, of a first vinyl monomer copolymerized with the diolefin, and one or more polymer shells, at least one of which shells is a vinylaromatic polymer or copolymer, the particles further having an average particle diameter no more than 250 nanometers and toluene swell index of from 13 to 45, preferably from 15 to 25.

The core/shell polymers are useful for modifying the properties of olefinic, aromatic addition and/or condensation resins, particularly poly(styrene).

EP 0 265 142 A3



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 87 30 9016

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	FR-A-2 304 645 (UNIROYAL INC.) * Claims 1,5-7,9-12 *	1-11	C 08 F 279/02 C 08 L 25/06
Y,D	EP-A-0 143 500 (DOW CHEMICAL) * Claims 1-7 *	1-11	
A	US-A-3 300 545 (MONSANTO CO.) * Abstract *	1-11	
A	FR-A-1 223 341 (U.S. RUBBER CO.) * Claims 1-6 *	1-11	
A	GB-A- 899 999 (MONSANTO CHEM. CO.) * Claims 1-12 *	1-11	
A	DE-A-3 425 458 (BASF) * Claims 1-2; page 4, lines 30-31 *	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 L C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-11-1989	Examiner OUDOT R.
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